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ABSTRACT

A theoretical study of the temperature dependence of the rate constants for model reacting systems has been carried out in an attempt to understand some recent experimental measurements which imply the existence of negative activation energies. A collision theory model and classical trajectory calculations are used to demonstrate that the reaction probability can vary inversely with collision energy for bimolecular reactions occurring on attractive potential energy surfaces. However, this is not a sufficient condition to ensure that the rate constant has a negative temperature dependence. On the basis of these calculations it seems unlikely that a true bimolecular reaction between neutral molecules will have a negative activation energy.

I. INTRODUCTION

In recent years experimental rate constant measurements of some apparent bimolecular reactions have resulted in the assignment of negative activation energies.¹⁻⁴ These so-called negative activation energies arise from the fitting of the experimental data to the Arrhenius equation:

$$K(T) = A \exp(-E_A/kT). \quad (1)$$

The pre-exponential factor A and activation energy E_A are constants determined in the fit. Several hypotheses can be advanced to explain the measurements: (I) The reactions proceed along attractive potential energy surfaces without energy barriers on which slower collisions are more reactive than faster ones;¹ (II) The reactions proceed via the formation of metastable intermediates and, thus, are not true bimolecular reactions; and (III) The experimental data contain systematic errors. The present paper is an examination of the first hypothesis. This examination is made in terms of collision theory and classical trajectory calculations using model potential energy surfaces. We first examine whether slower collisions can be more reactive than faster ones, and second, whether this effect is sufficient to result in negative activation energies.

Rate data for some reactions for which negative activation energies have been reported are given in Table I. Note that most of the data have been reported with extremely small uncertainty limits. It is only in the last few years that such precise measurements of very fast gas phase

reaction rates have been possible. This advance in chemical kinetics research has arisen largely because of the concern over the detrimental effect of anthropogenic halocarbons on the earth's ozone layer. Comparisons of the compendia of rate constants for stratospheric reactions from 1974 (Ref. 7) and 1977 (Ref. 8) reveal the extent and improved precision of the new body of chemical kinetics data. Of particular interest are the measurements of activation energies over the temperature range 200-500 K for some very fast reactions. Previously, uncertainties of 0.5 to 1.0 kcal/mole existed in most measured activation energies and the small negative activation energies of interest in the present work were lost in the experimental uncertainty.

The reactions listed in Table I can be analyzed in terms of the three possible explanations given above. A collision complex mechanism can be ruled out for reaction (R1) since the intermediate ClOO species is very weakly bound with respect to the products and could have only a very short lifetime.⁶ Therefore, the result of Zahniser and Kaufman,¹ if preferred over the experimental data of Clyne and Nip⁵ or the calculated results of Jaffe,⁶ would imply the existence of a negative activation energy in a true bimolecular reaction. On the other hand, (R2) probably does proceed via a complicated mechanism involving at least two metastable intermediates.⁹ Cox² has reported preliminary rate constants for reaction (R3). Since it is a hydrogen transfer reaction, a mechanism involving an intermediate complex seems unlikely. However, the $\text{NH}_2 + \text{NO}$ reaction (R4) undoubtedly does involve a complicated mechanism and the overall rate expression cannot be taken as being that of a bimolecular process.³ Davis et al.⁴ have reported negative activation energies for the reactions

of atomic oxygen with tetramethylethylene (TME) and (cis - 2 - butene), reactions R5 and R6, respectively. They suggested⁴ that these data could be explained by a kinetic model in which the energy dependence of the reaction cross section is proportional to a delta function centered on the threshold energy.

Thus, the observed rate constants for (R2) and (R4) can be explained in terms of complex mechanisms (hypothesis II). The rest of the data presented in Table I, if correct, must be explained in terms of a collision theory model in which slower collisions are more likely to react than faster ones (hypothesis I). In the present work, we examine such a model in detail to determine if it is capable of reproducing the observed reaction rate data.

In the next section, we define a suitable collision theory model and demonstrate the conditions that must be met for a negative activation energy to be realized. In Sec. III, we describe four model potential energy surfaces based on the $\text{C}_2\text{O} + \text{O}$ reaction (R1). These surfaces are used for classical trajectory calculations of reaction cross sections and rate constants which are described in Sec. IV. The resulting cross sections and rate constants are used to determine the reliability of the collision theory model and to determine whether negative activation energies should be computed for physically reasonable systems. The conclusions of this study are given in Sec. V.

II. ACTIVATION ENERGIES IN COLLISION THEORY

The Arrhenius activation energy of a chemical reaction is actually an empirical concept that arises from the fitting of experimental rate

constant data. In the case of a system with a single internal state (v,J) , the activation energy has been shown to be equal to the average translational energy for reactive collisions minus the average translational energy for all collisions.¹⁰ For the general case in which many reactant internal states are populated, one can show that E_A is the difference in average total energy between reactive collisions and all collisions. Thus, negative activation energies can occur if enhanced reagent energy inhibits rather than promotes reaction. In this section, we construct a collision theory model to describe bimolecular reaction kinetics and examine the resulting activation energy.

The activation energy is formally defined by inverting the Arrhenius rate constant expression [Eq. (1)]:

$$E_A = -k \frac{d \ln K(T)}{d(1/T)} . \quad (2)$$

This simple expression is generally not flexible enough to represent the variation of the rate constant over a large temperature range and a three-parameter expression is often used instead:¹¹

$$K(T) = BT^q \exp(-E'_A/kT) , \quad (3)$$

where B , q , and E'_A are varied to fit the experimental data. Substituting Eq. (3) into Eq. (2), we have

$$E_A = qkT + E'_A . \quad (4)$$

The first term in Eq. (4) arises from the temperature dependence of the preexponential factor of the rate constant and is thought to be responsible

for the observed negative activation energies of the reactions listed in Table I.

In order to examine the physical significance of q and E'_A we consider the collision theory rate constant for a thermal atom-diatom exchange reaction ($A+BC \rightarrow AB+C$):¹²

$$K(T) = Q_{v,J}^{-1} \sum_{v,J} (2J+1) \exp \left(-E_{v,J}/kT \right) \left(\frac{8}{\pi \mu_{A,BC}} \right)^{1/2} (kT)^{-3/2} \int_0^{\infty} S_r(E, v, J) \exp(-E/kT) E dE, \quad (5)$$

where $E_{v,J}$ and $Q_{v,J}$ are the BC vibration-rotation energy and partition function, respectively, $\mu_{A,BC}$ is the atom-diatom reduced mass, and S_r is the total reaction cross section for BC in the (v, J) internal state and collision energy E . The reaction cross section depends on the interatomic forces and must be determined by quantum or classical mechanical scattering calculations. For the purpose of this discussion, however, we define a simplified model cross section as follows:

$$\begin{aligned} S_r(E) &= 0, & E < E_T \\ S_r(E) &= aE^f, & E \geq E_T \end{aligned} \quad (6)$$

where the parameters a and f are independent of temperature and internal state (v, J) and E_T is the threshold energy. Substituting (6) into (5) and defining $x = E/kT$, we have

$$K(T) = a \left(\frac{8}{\pi \mu_{A,BC}} \right)^{1/2} (kT)^{f+1/2} \int_{x_T}^{\infty} x^{f+1} e^{-x} dx. \quad (7)$$

The integral in Eq. (7) is the incomplete gamma function $\Gamma(f+2, X_T)$.¹³

The activation energy defined in Eq. (7) can be shown to be

$$E_A = (f + 1/2)kT + \frac{E_T}{\Gamma\left(f+2, \frac{E_T}{kT}\right)} \left(\frac{E_T}{kT}\right)^{f+1} \exp(-E_T/kT) . \quad (8)$$

Thus, $q = f + 1/2$ and the second term in Eq. (8) represents a temperature dependent E'_A . The special case $f = 0$ is equivalent to the hard sphere cross section. This results in $q = 1/2$ and represents the $T^{1/2}$ "collision frequency" factor commonly used in rate constant expression.

Since $E_T \geq 0$, E'_A cannot be negative in this model [see Eq. (8)] and a negative activation energy can only arise if $f < -1/2$. For most chemical reactions, however, $E_T > kT$ and the second term in Eq. (8) usually dominates. The threshold energy E_T is approximately equal to the potential energy barrier which separates reactants and products.^{14,15} It is believed that there are no such barriers for the systems listed in Table I, however, in which case $E_T \approx 0$. Setting $E_T = 0$, the model rate constant for these reactions is given by

$$K(T) = a \left(\frac{8}{\pi \mu_{A,BC}} \right)^{1/2} (kT)^{f+1/2} \Gamma(f + 1/2) . \quad (9)$$

Equation (9) is finite for $f > -2$ and $E_A = (f + 1/2)kT$ is negative for $-2 < f < -1/2$. Thus, the cross section must have a strong inverse dependence on energy before a negative activation energy can be achieved. Since E'_A is physically similar to an activation energy one can say that

the rate constant given by Eq. (9) has a "zero activation energy" but a nonzero "temperature dependence" equal to $f + 1/2$.

In the above model, the case of $E_T = 0$ and $f < 0$ corresponds to the situation we are examining in the present study. For this case, slower collisions have larger cross sections; the larger cross sections mean they have greater probability of reacting than faster ones. However, only if $f < -1/2$ will a negative temperature dependence or Arrhenius activation energy result.

III. MODEL POTENTIAL ENERGY SURFACES

The calculation of reaction cross sections and rate constants requires knowledge of the potential energy surface of the system under study. Ab initio calculations of these surfaces are quite difficult and unnecessary for the purpose of the present work since we only want to study a general phenomenon in chemical kinetics. Thus, we have constructed four empirical potential energy surfaces for a generalized reaction $A+BC \rightarrow AB+C$. These surfaces have been modeled loosely after reaction (1) and have a potential well corresponding to the C_{200} equilibrium geometry¹⁶ which is 63.6 kcal/mole lower in energy than the reactants asymptote and 7.8 kcal/mole lower than the product asymptote. The potential energy is given by the sum of Morse potentials for the AB and BC bonds and a triatomic double minimum bending potential which is switched off as A and BC separate.

This bending potential takes the form

$$V_B(\theta_{ABC}) = F(R_{AB}) \left[A(\theta_{ABC} - \pi)^2 + \frac{B}{C + (\theta_{ABC} - \pi)^2} + D \right] \quad (10)$$

where $F(R_{AB})$ is the switching function

$$\begin{aligned} F(R_{AB}) &= 1, & R_{AB} < \rho - \delta\rho; \\ F(R_{AB}) &= 1/2 - \frac{\delta\rho (R_{AB} - \rho)}{(\delta\rho)^2 + (R_{AB} - \rho)^2}, & \rho - \delta\rho \leq R_{AB} \leq \rho + \delta\rho; \\ F(R_{AB}) &= 0, & R_{AB} > \rho + \delta\rho. \end{aligned} \quad (11)$$

Both the bending potential and the switching function have been discussed previously.⁶ The bending potential V_B is parameterized to reproduce the ClOO bond angle (110°) and bending force constant.¹⁶ The choice of ρ and $\delta\rho$ determine the range of R_{AB} over which the bending potential is switched on during A + BC collisions. If ρ is small then A + BC can approach close enough to feel substantial A - B attraction for any BC orientation. This case corresponds to the most attractive potential surface. If ρ is large the triatomic bending potential will dominate the kinetics and only collisions occurring over a small range of θ_{ABC} can be reactive. The width of this range of bond angles will be greater for collisions with higher collision energy, thereby introducing a positive temperature dependence to the reaction rate constant. Four potential surfaces differing only in the choice of ρ and $\delta\rho$ were used in the present study. In addition an exponential repulsion term for R_{AC}

$$V_{\text{REP}} = 5.0 \exp[-4(R_{\text{AC}}-1.6)] \quad , \quad (12)$$

where distances are in Å and energies in kcal/mole, was added to the potential energy expression to prevent R_{AC} from going to zero during A + BC collisions. The parameters used in constructing the potential energy surface are given in Table II.

The potential energy profile along a schematic reaction coordinate is shown in Fig. 1 along with the four ranges of R_{AB} spanned by the switching functions considered in the present study. Figures 2 and 3 are cuts through these potential energy surfaces $V(R_{\text{AB}}, \theta_{\text{ABC}})$ for the extreme cases (I and IV) at $R_{\text{BC}} = 1.83\text{Å}$. Note that in Case I (Fig. 2) A and BC can approach to $R_{\text{AB}} < 2.5\text{Å}$ without feeling any appreciable bending potential while in Case IV (Fig. 3) the V_{B} extends to $R_{\text{AB}} = 4\text{Å}$. The reactants are still at the asymptotic energy when $R_{\text{AB}} = 4\text{Å}$ but they are more than 2 kcal/mole down into the triatomic potential well when $R_{\text{AB}} = 2.5\text{Å}$. The rate constants for reactions occurring on these potential surfaces should exhibit strikingly different temperature dependences.

IV. CLASSICAL TRAJECTORY CALCULATIONS

Classical trajectory calculations have been performed to determine total cross sections and rate constants for reactions occurring on the model potential energy surfaces. These calculations will assess the validity of our premise and the collision theory model presented in Sec. II.

The quasiclassical trajectory method^{13,17} was used to compute the cross sections as a function of collision energy for the most attractive

model potential surface (Case I) at collision energies between 0.1 and 1.0 kcal/mole and BC internal energy state $(v,J) = (0,15)$. These conditions correspond to 0.624 kcal/mole vibrational energy and 0.308 kcal-mole rotational energy in BC. At each collision energy the cross section was based on the calculation of 250 trajectories with a maximum impact parameter of 5\AA . The resulting data, which are shown in Fig. 4, are well fit by $S_r = 27.0/E^{1/4} \text{\AA}^2$. Analysis of these calculations showed that slower collisions can be reactive over a larger range of impact parameters than faster ones. For example the largest observed impact parameter for a reactive trajectory decreased from 5.0\AA to 4.5\AA as E increased 0.1 to 1.0 kcal/mole. This substantiates the first part of our premise: namely, that the long-range attraction is more effective in promoting reaction at lower collision energies. Both the effective range of impact parameters and the total reactive cross sections are greater for slower collisions than faster ones. It now remains to be seen whether this effect can lead to a rate constant with a negative temperature dependence.

The phase space trajectory method^{6,18} was used to calculate thermal rate constants over the temperature range 200 K to 350 K for reactions occurring on each of the four potential energy surfaces. Each rate constant is based on a sample of 500 trajectories and has a standard error of 3.2 to 6.2% owing to the statistical sampling method used.

Arrhenius plots of these data are shown in Fig. 5. It can be seen that the rate constants for Cases I to III exhibit almost no temperature dependence while the data for Case IV have a definite negative slope. Least squares fits to these data for $\log K(1/T)$ yield activation energies

of 0.05, 0.00, and 0.01 kcal/mole for Cases I to III, respectively. Thus these rate constants exhibit a small positive or zero temperature dependence. For Case IV we obtain an activation energy of 0.28 kcal/mole by a similar procedure. If we assume the rate constant expression given by Eq. (3) with $E_A' = 0$ then $K \sim T^q$ where q is determined by least squares fitting to be 0.09, 0.00, 0.03, and 0.54 for the four cases, respectively. The calculated cross sections for Case I also indicate that $E_A' \sim E_T \approx 0$. Using these data in the collision theory model, we arrive at the prediction that $q = 0.25$.

The observed temperature dependences would indicate that $S_T \sim E^{-0.5}$ for Cases I to III according to the collision theory model presented in Sec. II. These results indicate that changes in the range of the bending potential do not seem to affect the temperature dependence of the rate constant or the form of the reaction cross section as long as the range of V_B does not exceed the range of the A-B attraction. For Case IV we have $S_T \sim E^{0.04}$. In this case the colliding reactants feel the bending potential before the onset of A-B attraction.

The agreement is quite satisfactory considering that the classical trajectory rate constants include contributions from a thermal distribution of reactant vibration-rotation levels while the cross sections were determined for a single arbitrary internal energy state. The results of the trajectory calculations, then, support the conclusions of the collision theory model. The probability of reaction can vary inversely with collision energy for systems with attractive potential energy surfaces. However, this is not a sufficient condition to ensure that the rate con-

stant will exhibit a negative temperature dependence for the potential energy surfaces considered.

V. CONCLUSIONS

The results of the total reaction cross section and rate constant calculations performed in this study demonstrate that slower collisions can lead to enhanced reaction probabilities. However, this fact by itself is not sufficient to cause a negative temperature dependence in the rate constant. Indeed, none of the rate constants computed in this study exhibited such a temperature dependence. In addition, the simple collision theory model presented here, which examines the relationships between cross sections and activation energy, seems to qualitatively account for all these results.

Thus, we conclude that the cross section must have a strong inverse dependence on collision energy in order for the rate constant to show a negative temperature dependence. Undoubtedly, the strength of the long-range force between reactants is an important factor. In ion-molecule reactions, where the intermolecular forces are stronger, the cross section will probably have a stronger inverse dependence on collision energy and negative activation energies will result.¹⁹ However, for neutral-neutral systems it seems unlikely that a true bimolecular rate constant will have a negative temperature dependence.

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TABLE I. RATE CONSTANT DATA FOR REACTIONS WITH NEGATIVE ACTIVATION ENERGIES.

Reaction	Temperature range (K)	Rate constant (cm ³ molecule ⁻¹ s ⁻¹)	Temperature Dependence ^a	Reference
(R1) ClO+O+Cl+O ₂	(a) 220-300	(3.38±0.50)×10 ⁻¹¹ exp[(75±40)/T]	T ^{-0.29}	Zahniser and Kaufman ¹
	(b) 220-426	(1.07±0.3)×10 ⁻¹⁰ exp[-(224±75)/T]	T ^{-0.75}	Clyne and Nip ⁵
	(c) 220-1000	4.36×10 ⁻¹¹ exp(-191/T)	T ^{-0.73}	Jaffe ⁶
(R2) ClO+NO+Cl+NO ₂	220-300	(1.13±0.14)×10 ⁻¹¹ exp[(200±30)/T]	T ^{-0.78}	Zahniser and Kaufman ¹
(R3) HO ₂ +HO ₂ →H ₂ O ₂ +O ₂	?	(1.4±0.7)×10 ⁻¹⁴ exp[(1651±205)/T]	?	Cox ²
(R4) NH ₂ +NO→N ₂ +H ₂ O	300-500	(1.0±0.2)×10 ⁻¹³ exp[525±100/T]	T ^{-1.25}	Lesclaux et al. ³
(R5) O+(CH ₃) ₂ C=C(CH ₃) ₂ → products	268-443	(5.58±1.07)×10 ⁻¹² exp[(785±60)/T]	T ⁻²	Davis et al. ⁴
(R6) O+(CH ₃)HC=CH(CH ₃)→ products	268-443	(9.69±0.96)×10 ⁻¹² exp[(160±30)/T]	T ^{-0.5}	Davis et al. ⁴

^a Defined according to $K(T) = BT^q$.

TABLE II. POTENTIAL ENERGY SURFACE PARAMETERS.

	D_e (kcal/mole)	R_e (Å)	β_e (Å ⁻¹)	
Morse parameters ^a				
AB	63.59	1.23	3.313	
BC	7.76	1.83	3.458	
V_B parameters ^b				
A	31.1327 kcal/mole			
B	192.0009 kcal/mole			
C	0.9908			
D	-123.7830 kcal/mole			
Case	I	II	III	IV
ρ , Å	2.0	2.5	2.5	2.5
$\delta\rho$, Å	0.5	0.5	1.0	1.5

^aParameters for ClO₂ from Arkell and Schwager.¹⁶

^bFrom Jaffe.⁶

FIGURE CAPTIONS

- FIG. 1. Schematic reaction path for the reaction $A + BC \rightarrow AB + C$. The limits of the switching regions ($\rho \pm \delta\rho$) of the attenuation factor used in the bending potential for the four model potential surfaces are shown.
- FIG. 2. Contours of equal potential energy in kcal/mole as a function of R_{AB} and θ_{ABC} for Case I. The limits of the switching region, $R_{AB} = \rho \pm \delta\rho$, are shown by dashed lines. Regions of the potential surface corresponding to reactants ($A + BC$) and intermediate complex (ABC) are shown. The BC bond length is held fixed at its equilibrium value of 1.83 \AA .
- FIG. 3. Contours of equal potential energy in kcal/mole as a function of R_{AB} and θ_{ABC} for Case IV. The entire plot falls within the limits of the switching region which is centered at $R_{AB} = \rho = 2.5 \text{ \AA}$. The BC bond length is held fixed at its equilibrium value of 1.83 \AA .
- FIG. 4. Quasi-classical trajectory reaction cross sections versus collision energy for Case I with $v = 0$, $J = 15$. The error bars reflect the statistical sampling error in the trajectory calculation. The solid curve is the least squares fit to the cross section data. $S_r \sim E^{-1/2}$ is shown for comparison. This is the relation which would give no temperature dependence according to the collision theory model.
- FIG. 5. Arrhenius plot of the phase space trajectory rate constant data for the four cases considered. The error bars reflect the statistical sampling error in the trajectory calculations. The curves are least squares fits to the rate constant data.

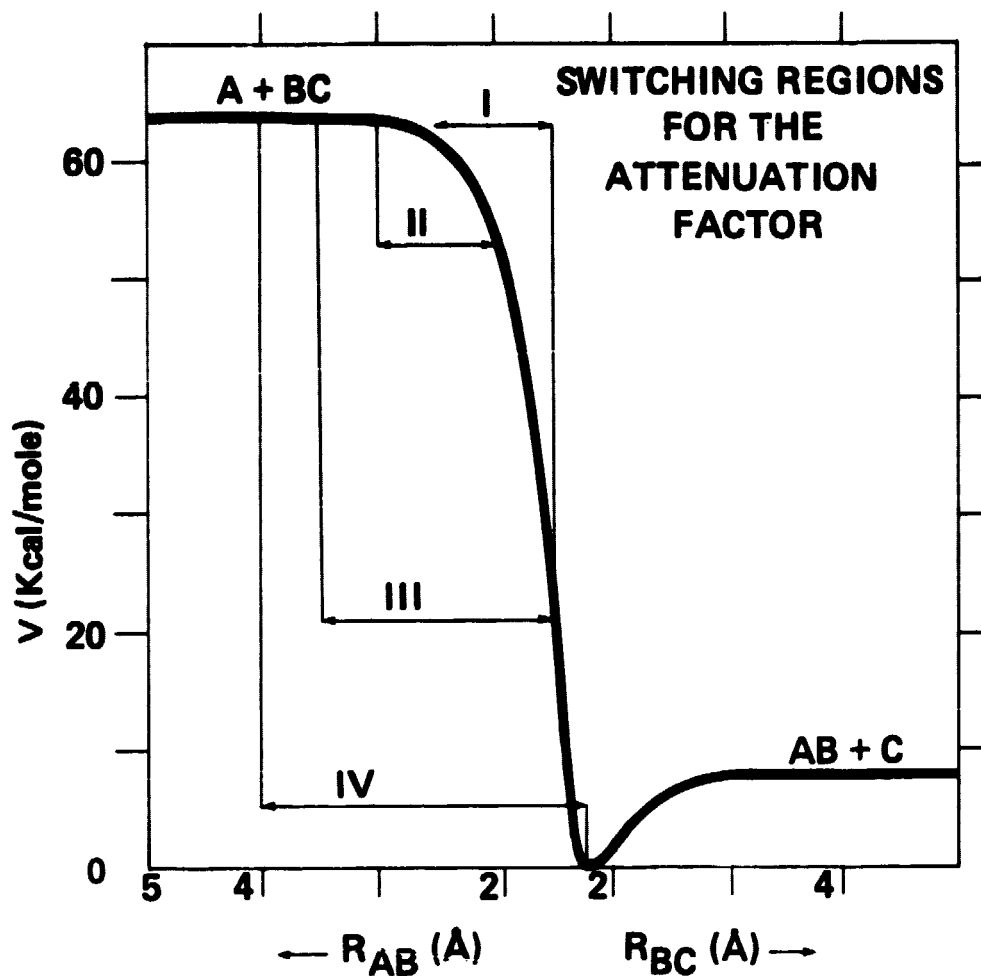


FIG. 1. Schematic reaction path for the reaction $A + BC \rightarrow AB + C$. The limits of the switching regions ($\rho \pm \delta\rho$) of the attenuation factor used in the bending potential for the four model potential surfaces are shown.

$V(R_{AB}, \angle ABC)$ for Case I

$R_{BC} = 1.83 \text{ \AA}$

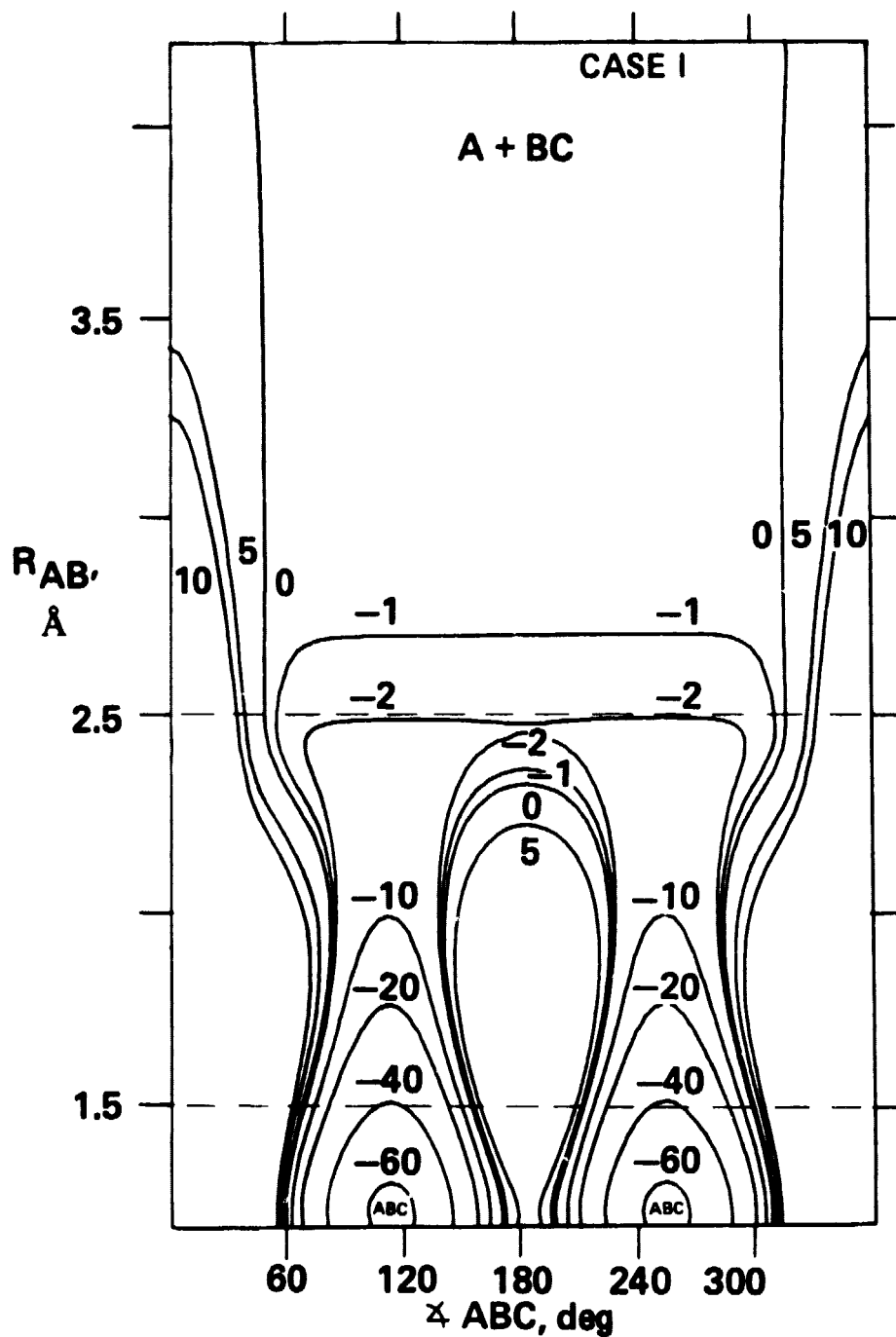


FIG. 2. Contours of equal potential energy in kcal/mole as a function of R_{AB} and $\angle ABC$ for Case I. The limits of the switching region, $R_{AB} = \rho \pm \delta\rho$, are shown by dashed lines. Regions of the potential surface corresponding to reactants (A + BC) and intermediate complex (ABC) are shown. The BC bond length is held fixed at its equilibrium value of 1.83 Å.

$V(R_{AB}, \angle ABC)$ for Case IV
 $R_{BC} = 1.83 \text{ \AA}$

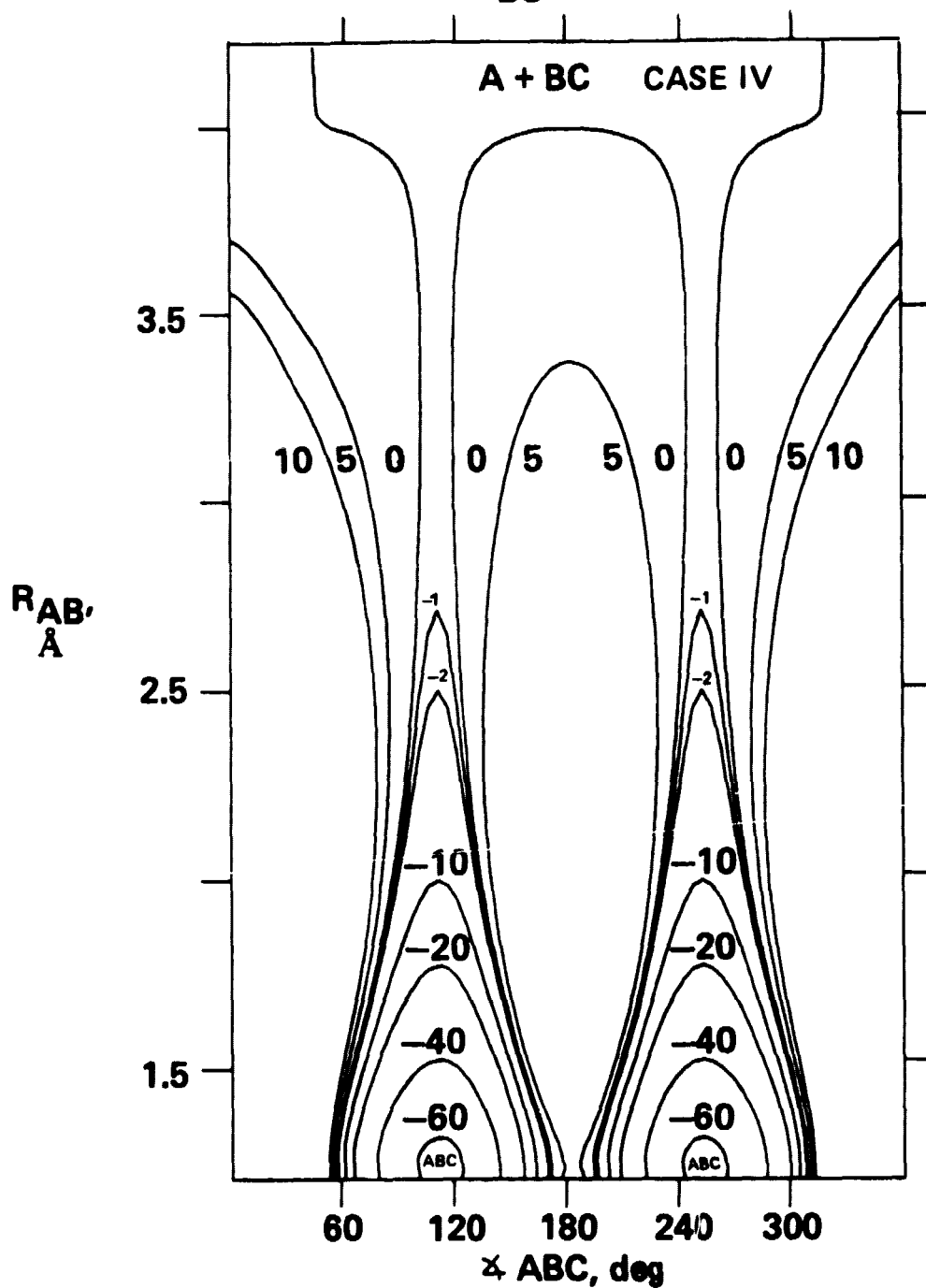


FIG. 3. Contours of equal potential energy in kcal/mole as a function of R_{AB} and $\angle ABC$ for Case IV. The entire plot falls within the limits of the switching region which is centered at $R_{AB} = \rho = 2.5 \text{ \AA}$. The BC bond length is held fixed at its equilibrium value of 1.83 \AA .

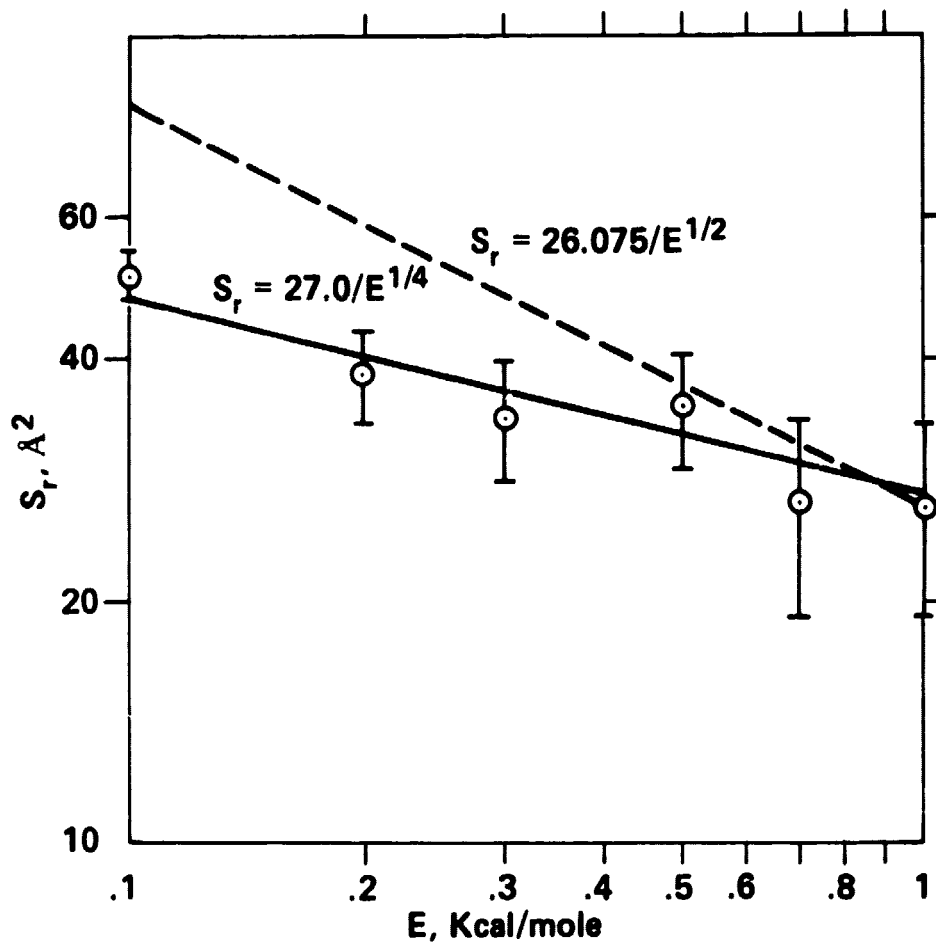


FIG. 4. Quasi-classical trajectory reaction cross sections versus collision energy for Case I with $v = 0$, $J = 15$. The error bars reflect the statistical sampling error in the trajectory calculation. The solid curve is the least squares fit to the cross section data. $S_r \sim E^{-1/2}$ is shown for comparison. This is the relation which would give no temperature dependence according to the collision theory model.

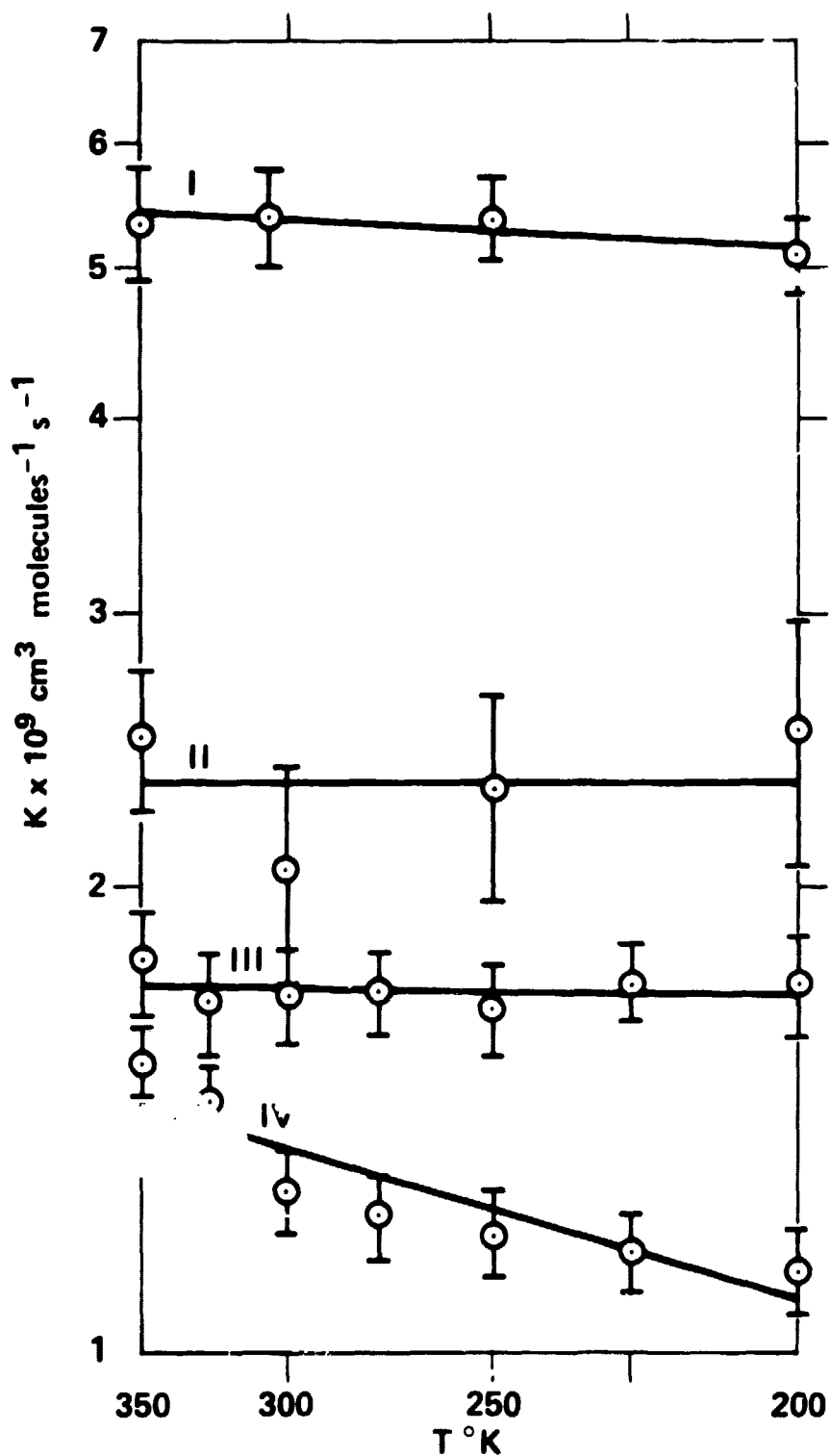


FIG. 5. Arrhenius plot of the phase space trajectory rate constant data for the four cases considered. The error bars reflect the statistical sampling error in the trajectory calculations. The curves are least squares fits to the rate constant data.